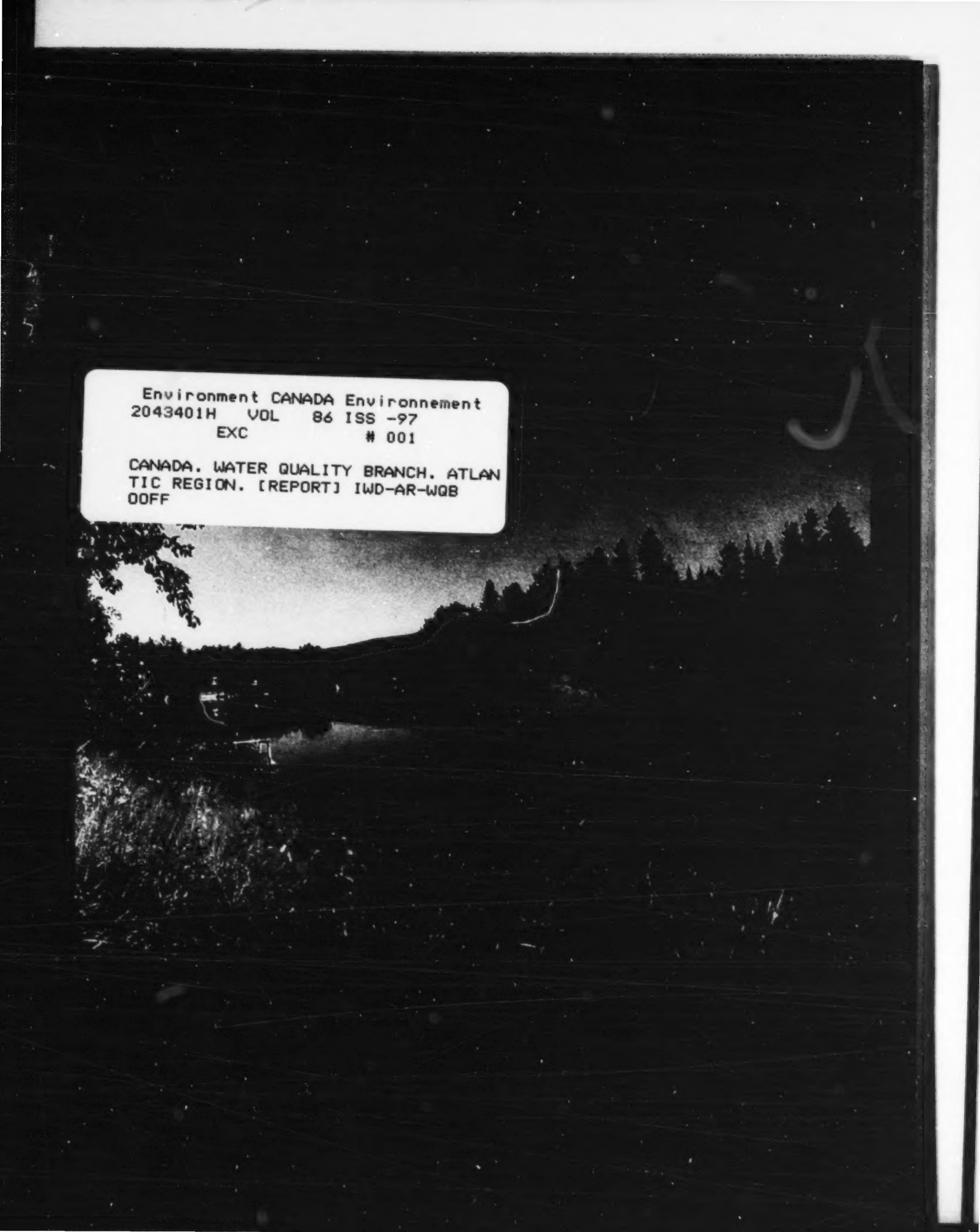


Environment CANADA Environnement
2043401H VOL 86 ISS -97
EXC # 001

CANADA. WATER QUALITY BRANCH. ATLAN
TIC REGION. [REPORT] IWD-AR-WQB
00FF

IWD Report No.

IWD-AR-WQB-86-97

This report has been submitted to
Water, Air & Soil Pollut. as part of
the Muskoka Acid Precipitation Proceedings,
and is subject to further revision

PATTERNS AND IMPORTANCE OF DISSOLVED ORGANIC CARBON IN FOUR ACIDIC BROWNWATER STREAMS IN NOVA SCOTIA, CANADA

by

T.A. Clair [1] and B. Freedman [2]

IWD-AR-WQB-86-97

1) Water Quality Branch, Inland Waters Directorate
Environment Canada, P. O. Box 861, Moncton
N. B., E1C 8N6

2) Institute for Resource and Environmental Studies,
and Department of Biology, Dalhousie University,
Halifax, N. S., B3H 4J1

ABSTRACT

The temporal variation and importance of dissolved organic carbon (DOC) was investigated in four brownwater streams in Nova Scotia, Canada whose basins received approximately 20 $kg.ha^{-1}.yr^{-1}$ of sulfate. Organic anions contributed an average of 23% of total anion equivalents, and mean volume-weighted annual average DOC closely paralleled mean annual pH among the four streams. However, within each waterbody, correlations of hydrogen ion with DOC were insignificant, whereas they were significant but weak with sulfate. DOC was consistently correlated with concentrations of polyvalent cations, suggesting that the latter may occur as organic complexes. Flux of DOC from the study streams was strongly related to water flow; variations of DOC concentration were of much less influence on rates of DOC flux.

INTRODUCTION

Southwest Nova Scotia receives approximately 20 $kg.ha^{-1}.yr^{-1}$ of sulfate from the atmosphere (Shaw 1979). A high proportion of these surface waters are acidic, and populations of Atlantic Salmon are exhibiting declining populations and reduced survival (Watt et al. 1983; Lacroix 1985; Lacroix et al. 1985). There is, however, controversy about the importance of anthropogenic influences on acidification in Nova Scotia, because of the common presence in surface waters of high concentrations of organic substances, (measured as dissolved organic carbon (DOC)), leached from bogs and soils. Because of high DOC levels, brownwater streams and lakes are considered by some to be naturally acidified, with soils neutralizing most of the atmospheric acid input (Krug et al. 1985).

The present report describes results of a study of four brownwater streams in Nova Scotia, chosen to provide a range of DOC levels. The problems being addressed include: i) the contribution of organic anions to total anion equivalents; ii) the correlation within each stream of variations of DOC with other ions, especially hydrogen and metals, and iii) the temporal variations of concentration and flux of DOC.

STUDY AREA AND METHODS

The study area is centred in Kejimkujik National Park, Nova Scotia, Canada (Figure 1). The terrestrial part of the study area is 94% covered by conifer, deciduous, and mixed forests. Bedrock is variable, but mainly granite, slates with quartzite, and greywacke (Gimbarzevsky 1975). The landscape has an almost continuous cover of shallow glacial tills, with frequent drumlin and moraine deposits. Typical surface waters in the study area are oligotrophic, and many are dark-coloured due to dissolved organic substances leached from podsols and Sphagnum and heath bogs in their watersheds.

The four study watersheds differ in size: the Mersey River is 295 km^2, Moose Pit Brook is 16.7 km^2, Whiteburn Brook is 9.5 km^2, and Rogers Brook 8.7 km^2. All have brown, organic waters, ranging from Moose Pit Brook with its particularly dark and acidic waters (mean annual DOC = 14.1 mg/L; mean annual pH = 4.6) to the relatively clearer Whiteburn Brook (DOC = 5.6 mg/L; pH = 5.6).

The Mersey River and Moose Pit Brook were gauged with standard Water Resources Canada automatic water level recorders. Rogers Brook and Whiteburn Brook had water height recorded manually using staff gauges, either daily or frequently. Water samples were collected at least weekly in clean, 1 L Nalgene bottles. All chemical analyses were done according to Standard Environment Canada NAQUADAT Procedures (Anonymous 1984). Note that sulfate was analyzed by ion chromatography. Organic

anions (OA-) were not measured directly, but were computed from DOC and pH, using the method of Oliver et al. (1983).

Collection of samples for this analysis began in June 1980 in the Mersey River, and March 1983 for the remaining streams. In all cases, the last samples used in this analysis were collected in March 1985.

OBSERVATIONS AND DISCUSSION

Cation concentration in these surface waterbodies was dominated by sodium (an average of 51% of total cation equivalents among the four streams), magnesium (17%), and calcium (16%) (Table I). Hydrogen ion accounted for only 4% (range of less than 1% to 9%) of total cation equivalents. Anions were dominated by chloride (averaging 53% of total anion equivalents). Because of the study area's proximity to the Atlantic Ocean (approx. 60 km), large amounts of sodium chloride are deposited from the atmosphere and show up in water. OA^- contributed an average of 23% of total anion equivalents and was the second most important anion in two of the streams. Sulfate contributed an average of 21% of anion equivalents.

Compared with non-organic fresh waters, organic anions are relatively important in the ionic chemistry of these streams as it is known that waters with high concentrations of DOC can be naturally acidic, usually in the pH range 4.0 to 5.0 (Clymo 1984; Gorham et al. 1984). Among our four study streams, mean annual acidity closely tracks mean annual DOC (Moose Pit Brook DOC = 14.1 mg/L, pH = 4.6; Mersey River DOC = 9.4 mg/L, pH = 4.9; Rogers Brook DOC = 7.3 mg/L, pH = 5.1; Whiteburn Brook DOC = 5.6 mg/L, pH = 5.6). This, in conjunction with the high contributions of organic anions to total anion equivalents, suggests that dissolved organic substances are partly responsible for the general acidity of these surface waters.

Statistical relationships between DOC and other chemical constituents within each waterbody were examined by bivariate correlation analysis (Table II). As expected, DOC correlated strongly with color. The correlation with OA^- is also expected, since DOC is the most important variable in the calculation of OA^- (note that DOC and OA^- are so strongly correlated that they can be used interchangibly. Other correlations with DOC were generally strongest for polyvalent cations, especially for Ca, Mg, Al, Fe and Mn (Table 2). The correlations of these with DOC suggests that they are probably occurring as organic complexes, rather than in ionic form. Clair and Komadina (1985) using the Campbell et al. (1983) chelation method, confirmed this relationship for aluminum by finding that virtually all of the total extractable aluminum in these four waterbodies was non-labile, and probably bound to dissolved organic matter. In this form Al is much less bioavailable and toxic (Baker and Schofield 1982). This is an important difference between acidic waters high in DOC, and clear acidic waters.

Within the data set for each waterbody, variations of concentration of hydrogen ion are not correlated with variations of DOC (Table 2). This is contrary to our earlier observation that the relative average acidity of these brownwater streams was related to their relative concentration of organic anions. In fact, hydrogen ion was not consistently strongly correlated with any ionic constituent in Table 2. However, the anion that was most consistently correlated with hydrogen was sulfate (Mersey River $r = 0.799$, $p < 0.001$; Moose Pit Brook $r = 0.378$, $p < 0.001$; Rogers Brook $r = 0.431$, $p < 0.001$; Whiteburn Brook r =

0.282, $p < 0.01$). Except for the Mersey River, these correlations are rather weak, and account for little of the variation of hydrogen ion concentration. Nevertheless, it is noteable that sulfate is the most useful anion for explaining variations of hydrogen ion, even in these study streams, where organic anions play a major role in water chemistry. Mineral acidity thus appears to be more important than organic acids in describing short term changes in basin pH.

Temporal variation of water discharge in all four streams is similar to that displayed in Figure 2 for Mersey River, though the magnitude of discharge obviously varies amongst them. The very strong seasonality in discharge occurs in spite of small seasonal variations in mean monthly precipitation (Watson 1977). During the growing season, low runoff is largely due to high rates of evapotranspiration and storage in soils. During the early part of the high flow period, extending from November to mid-May, flow events occur in response to large precipitation events since soils are saturated. Later on, flow events occur in response to either rain input (as opposed to snowfall) or snowmelt events. However, mean daily water flow remains fairly high throughout November to mid-May, because the moderate Nova Scotian winter climate procludes deep accumulation of snowpack.

A strong seasonality of DOC (or OA^-) concentration is also apparent in all four water bodies (Figures 3a, b, c, d). In all of the streams, the tendency is for DOC concentrations to be highest during the low-flow period, i.e. having the largest relative impact on water chemistry in the summer. This trend is most marked for Moose Pit Brook

(Figure 3b), Rogers Brook (Figure 3d), and Whiteburn Brook (Figure 3c). In the larger Mersey River (Figure 3a) there is a tendency for high DOC concentrations to persist into the beginning of the high-flow period probably because of lag time between runoff from first order streams to the collection site. These patterns result in significantly negative correlations between water flow and DOC concentration (Table 2). However, the relatively weak nature of these correlations (the maximum amount of variation accounted for was 28%) indicates that particular streamflow episodes were not always accompanied by DOC concentration events. Since in the smaller streams respond more rapidly to rain or snowmelt, the correlations were stronger than for the much larger Mersey basin.

Variations of flux of DOC (see Table 1 for flow-weighted average annual fluxes) are strongly controlled by variations of water flow in these streams. This is indicated in Table 2 by the relatively strong correlations of DOC flux and water flux, accounting for a range of 59% to 84% of the variation. Variations in DOC concentration are of much less influence on DOC flux, as indicated by their very weak correlations in Table 2, which account for <6% of the variation. Note, however, that this is not a strictly appropriate application of correlation analysis, since the variables being investigated are not statistically independent (i.e. since DOC flux is calculated as the product of DOC concentration times water flow, it is not proper to then regress DOC flux against these variables). Nevertheless, this simple analysis allows the calculation of a statistic which clearly quantifies the relationships among these variables. As such, it is a useful procedure,

although its statistical limitations must be recognized.

In summary, we find that metals such as aluminum correlate fairly well with DOC. This indicated complex formation that renders the aluminum non-labile. DOC concentration varies seasonally, with a pronounced trend to higher levels during the low-flow period of the growing season. However, by far the strongest influence on rate of DOC export from basins is rate of water flow. Though mean annual pH closely tracks average DOC among the four brownwater study streams, the within-stream variations of hydrogen ion are most strongly correlated with sulfate concentration. Thus, while the overall acidic character of these organic surface waters is due to DOC, within basin acidity changes are most likely due to variations of mineral acids.

ACKNOWLEDGEMENTS

The authors acknowledge the help of F. Luxton, U. Prager, C. Stewart and L. Boulter in data collection and analysis. T. Pollock critically reviewed the manuscript and the staff at Kejimkujik National Park for providing access to their facilities.

REFERENCES

Anonymous: 1984, 'NAQUADAT Dictionary of parameter codes'. Water Quality Branch, Environment Canada, Ottawa, 319 pp.

Baker, J.P. and Schofield, C.L.: 1982, Water, Air and Soil Pollut., 18, 289.

Campbell, P.G.C. et al.: 1983, Anal. Chem., 55, 2246.

Clair, T.A., et al.: 1982, 'Acid precipitation sensitivity of Canada's Atlantic Provinces. Tech. Bull. 124, Inland Waters Directorate, Environment Canada, Ottawa.

Clair, T.A. and Komadina, V.: 1984, 'Aluminum speciation in waters of Nova Scotia and their impact on WQB analytical and field method'. Tech. Rep. IWD-AR-WQB-84-69. Environment Canada, Moncton, N.B.

Clymo, R.S.: 1984, Phil. Trans. R. Soc. Lond. 305, 487.

Gimbarzevsky, P.: 1975, 'Biophysical survey of Kejimkujik National Park'. Information report FMR-X-81. Forest Management Institute. Petawawa, Ont.

Gorham, E. et al.: 1984, Can. J. Fish. Aquat. Sci. 41, 1256.

Krug, E.C. et al.: 1985. J. Air Pollut. Control Fed., 35, 109.

Lacroix, G.L.: 1985, Can. J. Fish. Aquat. Sci. 42, 292.

Lacroix, G.L. et al.: 1985, Can. J. Fish. Aquat. Sci. 42, 768.

Oliver, B.G. et al.: 1983, Geochim. Cosmochim. Acta, 47, 2031.

Shaw, R.W.: 1979; Env. Sci. technol. 13, 406.

Watson, W.B.: 1977, 'The climate of Kejimkujik National Park, Nova Scotia'. Project Report 26. Atmospheric Environment Service, Environment Canada. Toronto, Ont.

Watt, W.D. et al.: 1983, Can. J. Fish. Aquat. Sci. 40, 462.

TABLE I SELECTED WATER CHEMISTRY OF THE FOUR STUDY STREAMS - CONCENTRATION DATA ARE FLOW-WEIGHTED ANNUAL MEANS

	MERSEY RIVER	MOOSE PIT BROOK	ROGERS BROOK	WHITEBURN BROOK
Concentration (ueq/L)				
Ca	44.9	41.9	46.4	57.9
Mg	44.4	46.1	50.2	54.3
Na	141.4	118.8	137.5	197.5
H	12.0	25.0	8.1	2.3
Fe	7.5	7.2	14.3	7.2
Al	20.0	21.1	12.2	7.8
SO_4	54.3	52.8	64.5	55.7
Cl	144.1	107.4	135.4	203.0
OA	69.7	98.0	47.7	37.1
Anions/cations*	0.97	0.96	0.95	0.94
DOC (mg/L)	9.4	14.1	7.3	5.6
TC (mg/L)	14.3	21.1	14.4	10.7
pH	4.9	4.6	5.1	5.6
Flux (kg $ha^{-1}.yr^{-1}$)				
DOC	78	136	73	51
TC	118	203	150	103

* includes some minor constituents not reported here.

TABLE II CORRELATIONS BETWEEN WATER DOC CONCENTRATION IN WATER AND SELECTED CONCENTRATIONS OR FLUXES. * = p less than 0.001; ** = p less than 0.01

	MERSEY RIVER (n=992)	MOOSE PIT BROOK (n=103)	WHITEBURN BROOK (n=105)	ROGERS BROOK (n=230)
DOC x colour	0.690*	0.895*	0.816*	0.866*
x Na	0.424*	0.671*	0.179	0.525*
x Mg	0.668*	0.623*	0.311**	0.671*
x K	0.047	0.447*	0.181	0.481*
x Ca	0.533*	0.730*	0.439*	0.756*
x Cl	0.352*	0.255**	-0.094	0.040
x SO_4	-0.071	-0.543*	0.475*	-0.057
x Al	0.664*	0.865*	0.400*	0.825*
x Mn	0.200*	0.631*	0.525*	0.668*
x Fe	0.395*	0.898*	0.764*	0.719*
x H	0.029	0.149	-0.122	-0.109
x OA^-	0.973*	0.990*	0.948*	0.988*
X water flow	-0.283*	-0.460*	-0.533*	-0.493*
x DOC flux	0.042	0.001	-0.226*	-0.086
DOC flux x water flux	0.907*	0.766*	0.917*	0.846*

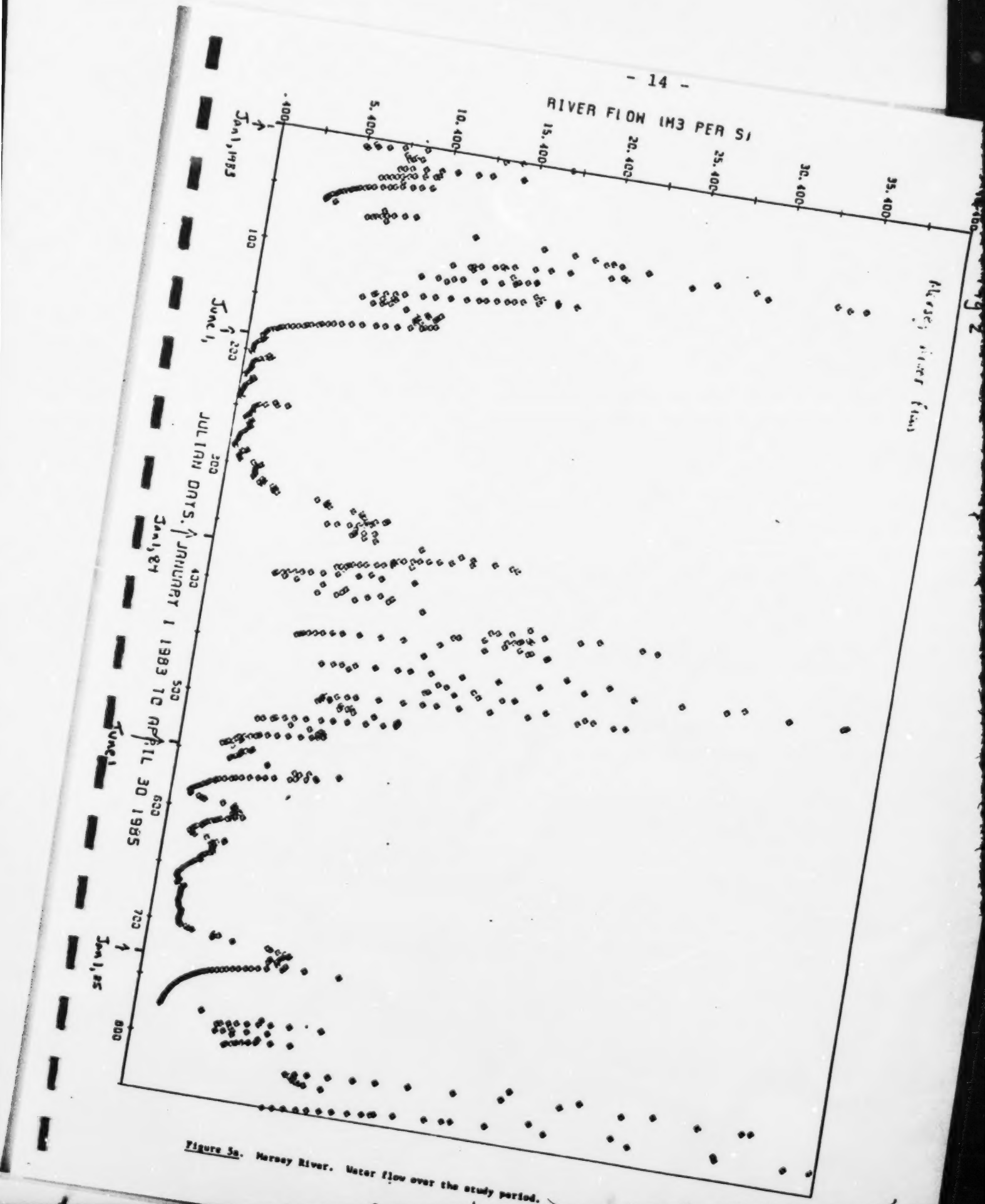


Figure 5a. Harvey River. Water flow over the study period.

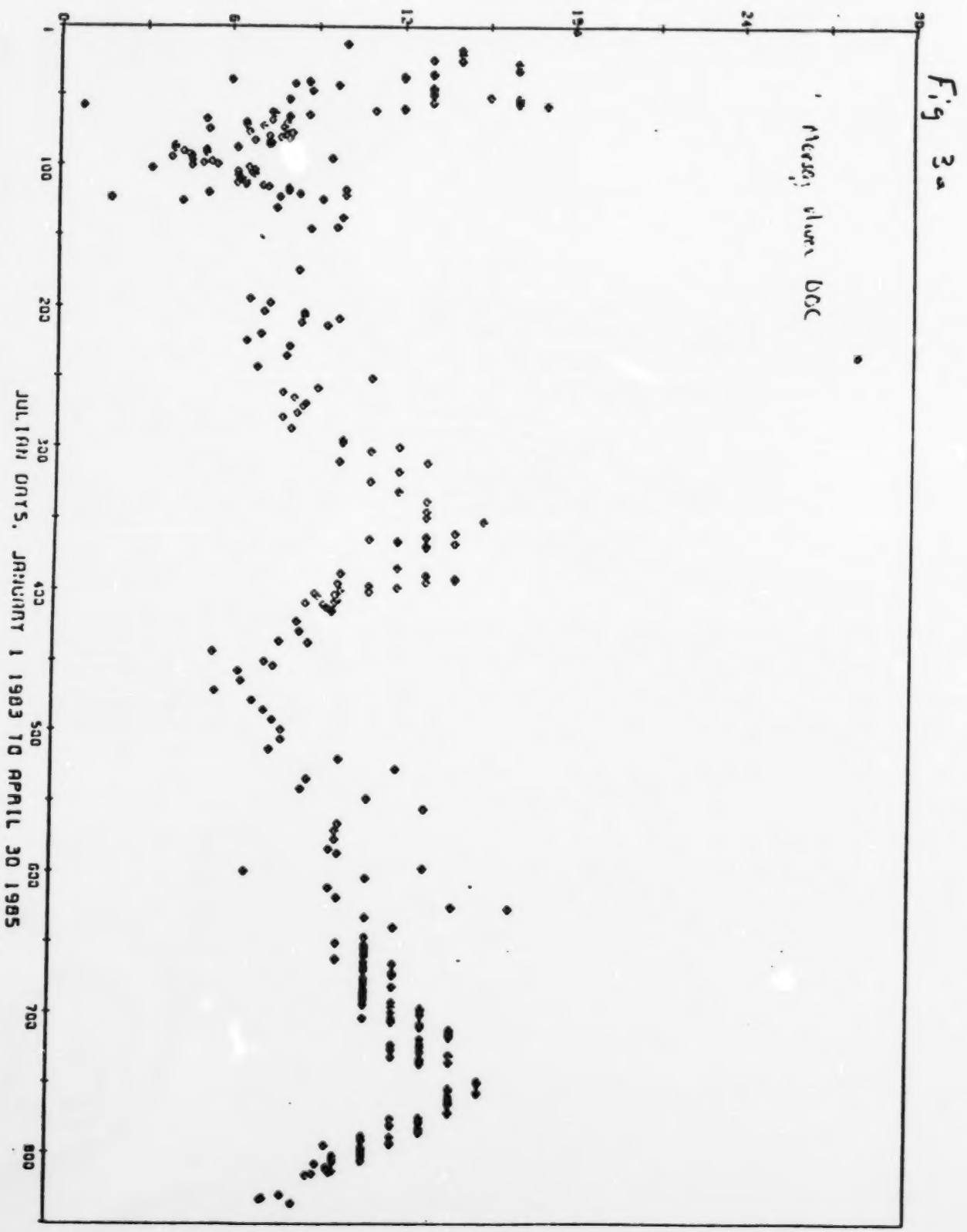
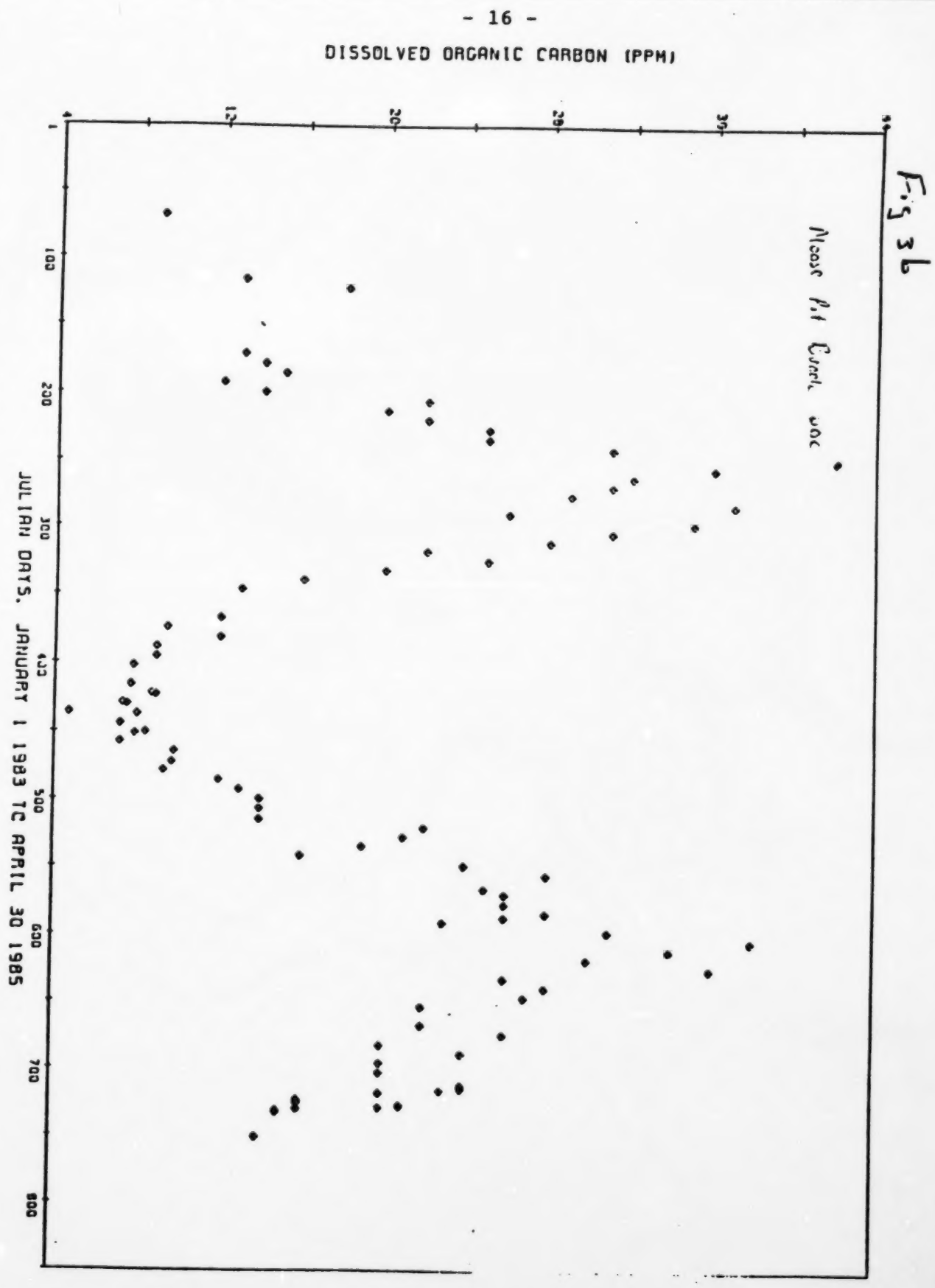


Figure 3f. Nersey River. Dissolved organic carbon over the study period.



Appendix 7f. Moosepit Brook. Dissolved organic carbon over the study period.

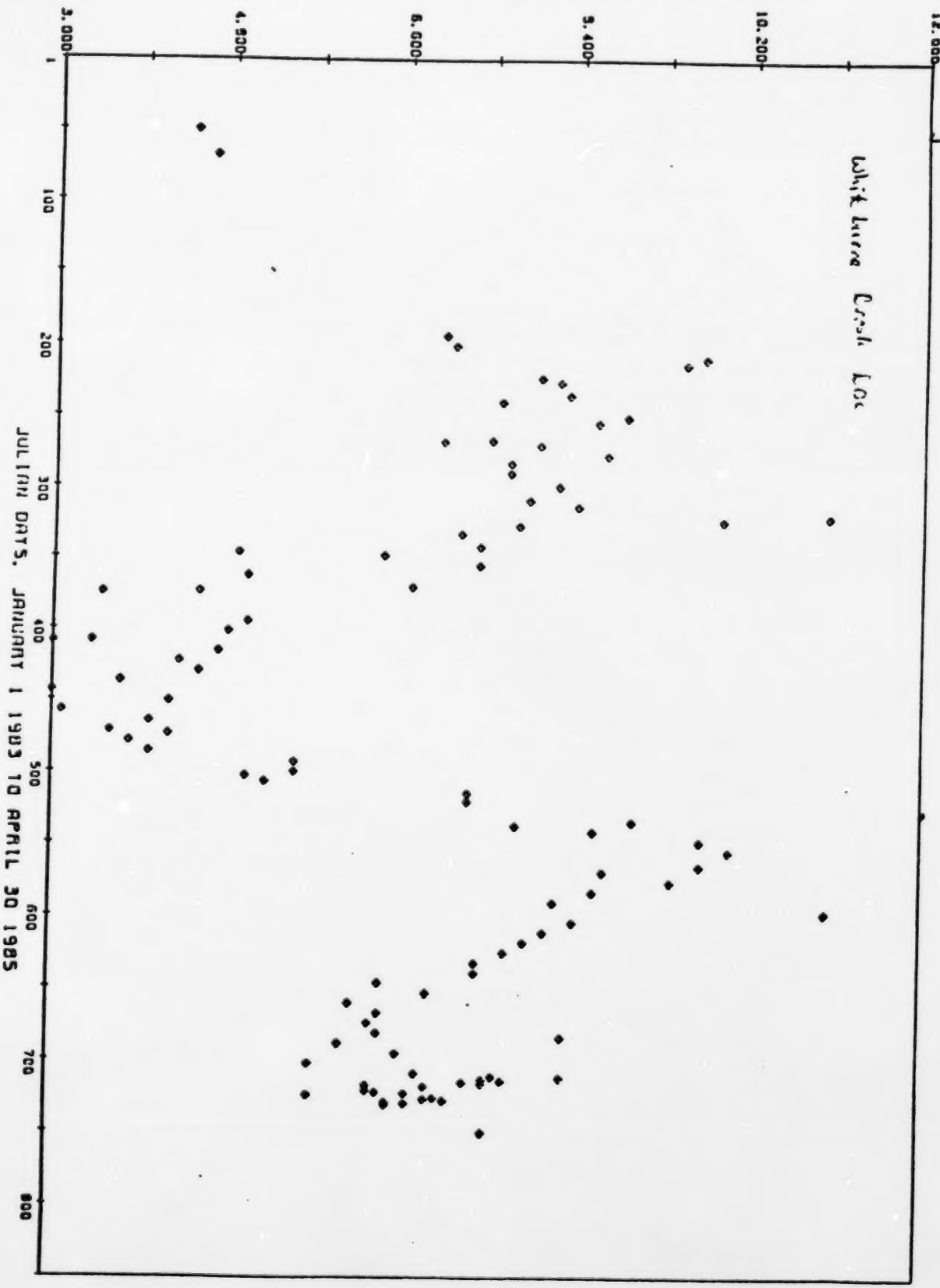


Fig 3c

Whiteburn Brook Loc

Appendix 8f. Whiteburns Brook. Dissolved organic carbon over the study period.

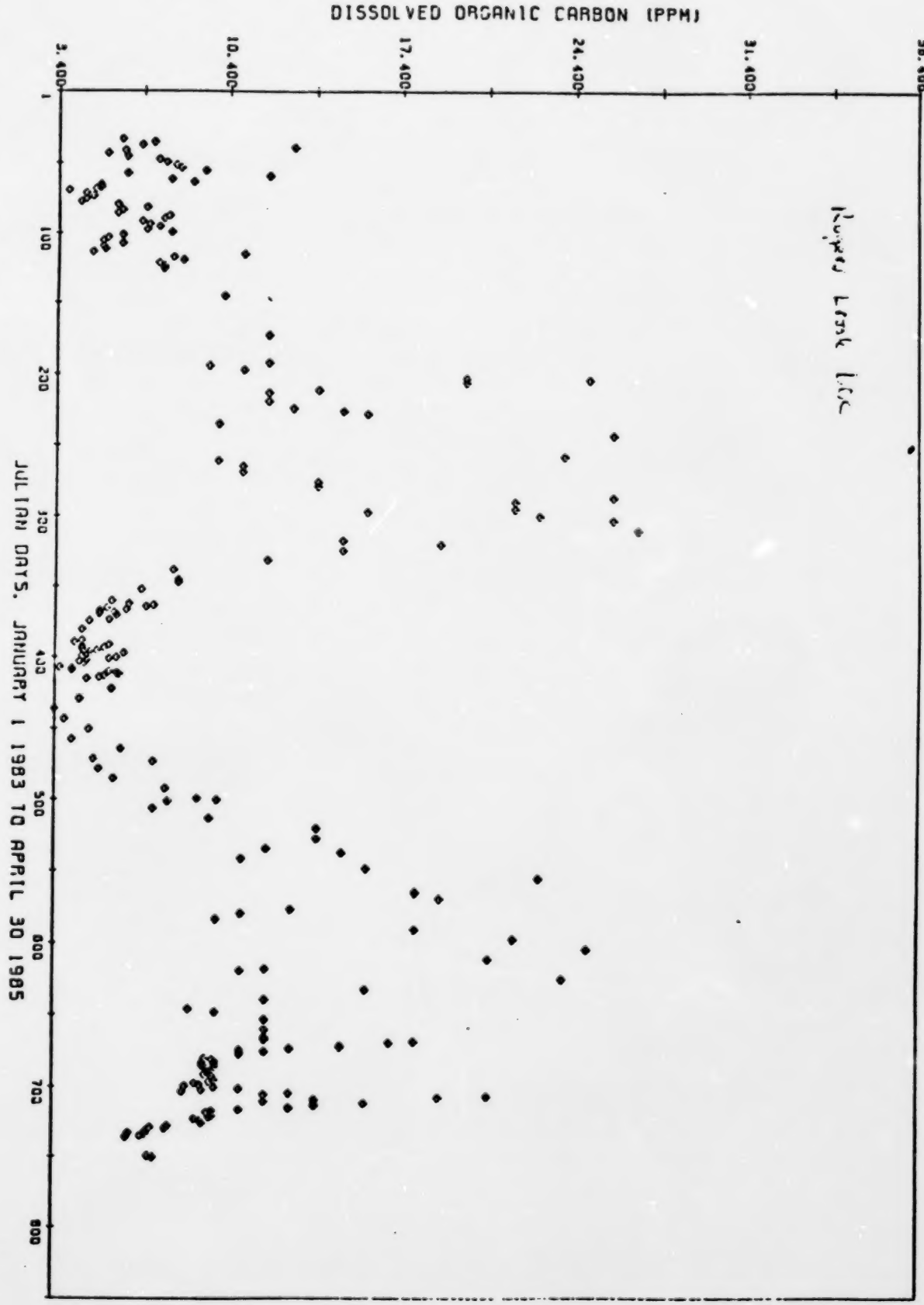


Fig 3f

Rogers Brook

Appendix 9f. Rogers Brook. Dissolved organic carbon over the study period.